# TEMPERATURE DEPENDENT RHEOLOGY OF SURFACTANT-HYDROXYPROPYL CELLULOSE SOLUTIONS

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The rheology of 1-8% hydroxypropyl cellulose (HPC) solutions has been studied in the temperature range of 20-45 degrees Celsius. The results showed that the relative viscosity at each HPC concentration decreases with increasing temperature. The relative viscosity decreases drastically at about 43 degrees Celsius due to a phase transition. The influence of anionic surfactant, sodium dodecylsulfate (SDS), induced gelation of a 2% HPC solution. The HPC solutions gelled at surfactant SDS concentrations ranging from 0.4 to 1.0 critical micelle concentration (CMC). The gelation of the HPC/SDS hydrogel is explained in the surfactant SDD – bridged HPC linear polymer chains. The complex viscosity – concentration profile was determined below the CMC of the SDS – water pair. The peak itself was a function of frequency indicating the presence of two relaxation times within the gelled network.

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# CHAPTER 1
# INTRODUCTION

The rheological properties of the addition of surfactants to polymer solutions have been widely studied. Depending on the type of polymer solution and surfactant, different properties of the resultant gel can be achieved. Specific gel properties can be utilized in various industrial and pharmaceutical applications. One area of increased interest is in low concentration gels.

## Rheology

Rheology is a widely known analytical technique that is used in studying the viscosity, modulus, and shear parameters of various systems. Several definitions and key relationships need to be discussed in order to understand how the rheological measurements were interpreted. Rheology is defined as the study of the flow and deformation of material.[1,2,3,4] One of the main components of rheology that is studied is the viscosity, $\eta$, which is the measurement of the resistance to continuous deformation, or flow. The stress, $\sigma$, is related to the rate of deformation through equation 1.

$$\sigma = \eta \overset{o}{\gamma}^{n} \tag{1}$$

When n=1, there is no shear rate dependence on shear stress implying a Newtonian fluid. The relative viscosity, $\eta_{Rel}$, is the viscosity of the solution, $\eta$, divided by the viscosity of the solvent, $\eta_{0,}$ as seen in equation 2.

$$\eta_{Rel} = \eta/\eta_0 \tag{2}$$

The specific viscosity is the relative viscosity minus unity as seen in equation 3.

$$\eta_{sp} = \eta_{Rel} - 1 \tag{3}$$

The intrinsic viscosity is the specific viscosity divided by the dispersed-phase concentration at very low concentrations and/or shear rates as seen in the relation in equation 4.

$$[\eta] = \lim_{C\to 0} \lim_{\gamma\to 0} \eta_{sp}/C \quad (4)$$

The apparent viscosity is the viscosity determined for a non-Newtonian fluid without reference to a particular shear rate for which it applies. There are two modes of viscosity measurement: oscillatory and rotational. In rotational testing the driving force for measuring the resistance to deformation is a shear rate, which is related to the velocity of the fluid. In oscillatory measurements, the applied deformation is a frequency. The oscillatory shear stress, $\sigma^*$, and resultant shear strain, $\gamma^*$, are defined in equation 5 and equation 6.

$$\sigma^* = \sigma_0 e^{j\omega t} \quad (5)$$

$$\gamma^* = \gamma_0 e^{j(\omega t - \Phi)} \quad (6)$$

The resulting modulus is complex given by equation 7, where the real part G' is the storage modulus and the loss modulus, G'', is given by equations 8 and 9 respectively.

$$G^* = \sigma^*/\gamma^* = G'(\omega) + jG''(\omega) = G' + iG'' \quad (7)$$

$$G' = \omega\eta'' \quad (8)$$

$$G'' = \omega\eta' \quad (9)^{2,3,4}$$

The viscosity is also complex, related to the complex shear modulus by equation 10. Comparing equations 10 and 11 we get equations 12 and 13 for the real and complex viscosity.

$$\eta^* = G^*/j\omega = G'(\omega)/j\omega + jG''/j\omega \quad (10)$$

$$\eta^* = \eta' + j(\eta'') \quad (11)$$

$$\eta' = G''/\omega \quad (12)$$

$$\eta'' = G'(\omega)/\omega \quad (13)^{1,2,3,4}$$

A material is termed shear thickening when the viscosity of a non-Newtonian fluid increases as the applied shear rate increases. This type of fluid is called a dilatant fluid. A material is termed shear thinning when the viscosity of a non-Newtonian material decreases as the applied shear rate increases. This type of fluid is called a pseudoplastic fluid. Pseudoplastic behavior may occur in the absence of yield stress as well as after the yield stress in the system has been exceeded. A system is termed thixotropic when the pseudoplastic flow is time dependent. Therefore, at a constant applied shear rate, viscosity gradually decreases, and a flow curve hysteresis occurs. In other words, after a given shear rate is applied and then reduced, some amount of time is needed for the original dispersed species alignments to be restored.[1,2,3,4]

Elastic materials are those that will return to their original shape after a deformation stress has been removed. An inelastic, or purely viscous material, will not return to its original shape after a deformation stress has been removed. Materials that exhibit both elastic behavior as well as inelastic behavior are termed viscoelelastic materials. When a material behaves in a manner consistent with the linear relation $\sigma = \eta\gamma'$ then it is considered a Newtonian fluid. A material that does not behave linearly according to equation 1 is considered non-Newtonian.[2,3,4,5]

# CHAPTER 2

# POLYMER SOLUTIONS

The rheological and mechanical properties of many polymers have been studied and documented. Both ionic and non-ionic polymers have been documented in the literature. Some of the more widely studied polymers have been hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), hydroxyethyl cellulose (HEC), ethyl hydroxyethyl cellulose (EHEC), sodium carboxymethyl cellulose (Na-CMC), poly (N-isopropylacrylamide) (P NIPA), gelatin, and various other cellulose derivatives. The cellulose derivatives share many of the same characteristics. Many of these polymeric systems as well as various methods to study these systems will be discussed in this paper.

Polymers are long chain molecules that are composed of smaller repeating units called monomers. These monomers are covalently bonded together and have at least two bonding sites, which are necessary to form the long chains.[5] Ionic polymers are those that exhibit ionic character. Non-ionic polymers are those that do not exhibit ionic character. Polymers can be formed via several different mechanisms including: step growth polymerization, free radical addition polymerization, ionic polymerization and copolymerization.[5]

## Hydroxyethyl Cellulose, HEC

One method used to examine the mechanical properties of polymeric systems is texture profile analysis, TPA. David Jones and coworkers used this method to examine the mechanical properties of HEC.[6,7,8] TPA consists of depressing a solid analytical probe into a gel at a preset depth and rate. Force-time plots of the depressions can be translated to study the hardness, adhesiveness to the probe, and compressibility of the

system, in this case, HEC. The results show that as the concentration of HEC (%w/w) increases, the hardness, adhesiveness to the probe, and compressibility of the sample increases as well. In similar testing of Na-CMC systems, the same tendencies were also observed.[7]

Subsequent rheological studies of the HEC polymer solution show that the storage modulus, G′, loss modulus, G″, and dynamic viscosity, η′, increase with increasing concentration, while the loss tangent decreases with increasing concentration. As the frequency of the system is increased, the storage modulus increases, while the dynamic viscosity and loss tangent decrease. Loss modulus increases up to 0.1 Hz at which point it behaves independently of the frequency.[7]

Sodium Carboxymethyl Cellulose, Na-CMC

In the Na-CMC system G′, G″, and η′ increase as Na-CMC concentration increases. The loss tangent does not change significantly as the concentration of Na-CMC increases. The frequency behavior of the Na-CMC system predictably shows that G′, and G″ increases with increasing frequency. Dynamic viscosity decreases with increasing frequency, and the loss tangent shows no effect to the frequency change. For both systems, the increase in G′ with increasing frequency indicates an increase in elastic behavior.[7]

These results are consistent with the Maxwellian description of the response of viscoelastic materials to oscillatory stresses. At high frequencies the gels behave as elastic solids. As frequency decreases, the materials display properties characteristic of both solids and liquids.[9] Except for the dilute systems, both HEC and Na-CMC gels showed elastic behavior. This is evident from the greater magnitude of G′ to G″. The

rheological results show that the HEC system has viscoelastic properties that are more frequency dependent than the Na-CMC system. The decreases in the dynamic viscosity, $\eta'$, with increasing frequency is characteristic of viscoelastic systems.[10,11]

## Ethyl(hydroxyethyl) Cellulose, EHEC

Ethyl(hydroxyethyl) cellulose, EHEC, steady flow viscosity vs. shear rate curves were studied by Anders Carlsson and colleagues. The results show that the viscosity decreases with increasing shear rate and with increasing temperature. This behavior in EHEC suggests a high tendency towards shear thinning, which is a characteristic of pseudo-plasticity.[12]

## Hydroxypropyl Cellulose, HPC

Several subsequent studies have looked at the rheology, specifically the viscosity characteristics of HPC solutions.[13,14,15,16] Different concentrations of HPC (25 wt. % - 55 wt. %) were subjected to shear rate experiments. In each case the viscosity decreased as the shear rate increased, and the viscosity increased as concentration increased up to about 40 wt.%. Above 40 wt. %, the viscosity decreased as the polymer concentration increases. It is believed that at concentrations of 45 wt.% and above, the solution is a liquid crystalline mesophase. For concentrations below 45 wt.%, the solution is biphasic. Each study showed that the HPC solutions exhibited a three region flow curve with shear thinning dominating at high shear rates (Region III). The Region III shear thinning reflects nonlinear viscoelastic effects.

# CHAPTER 3

# SURFACTANTS

A surfactant is a component that can alter the physical properties of the polymer system. There are three general types of surfactants, and are classified as nonionic, cationic, and anionic. Nonionic surfactants generally exhibit no significant interaction with the polymeric system. Cationic surfactants do not adsorb on the polymeric systems at lower concentrations. Anionic surfactants do adsorb on polymeric systems at lower concentrations, and therefore increase the relative viscosity of the bulk solution.[1] One common anionic surfactant is sodium dodecyl sulfate, SDS. Concentrated surfactant systems can still possess viscosities similar to those of the solvent. Dilute surfactant systems can be highly viscous compared to the solvent. These behaviors can be attributed to the flow characteristics in the solutions resulting from the different micellar structures formed from surfactant addition. The surfactant addition results in globular micelles in the concentrated system. The particles in this system are not connected allowing for the low viscosities. A network of aggregated micelles dominates the dilute system thereby allowing for the increased viscosities.[1]

## Quarternary Ammonium Surfactant Mixture, QASM

Rheological properties such as shear stress, yield stress and viscosity of cationic surfactant gels have been studied.[17] The primary cationic surfactant examined was an ammonium salt mixture called quarternary ammonium surfactant mixture, QASM. QASM was preheated to 50ºC and mixed with deionized water also preheated to 50ºC. The amount of water was altered to obtain different % w/w concentrations of QASM gels.

Shear stress/shear rate curves of QASM at varying concentrations were examined. For concentrations under 19% w/w the shear stress varied smoothly with increasing shear rate, which is a characteristic of liquid-like systems. At concentrations of 19% w/w and above, a yield stress was observed, which was shown by a sharp increase in the rate of deformation above a certain value. This indicates that above 19% w/w the system becomes gel-like and does not flow under small stresses. The system will begin to flow more easily above the yield stress. There also was a nonmonotonic change in the slope resulting in a shoulder in the stress/rate curve. The shoulder indicates a discontinuous flow-induced increase in the apparent viscosity. For ramp times from 5 to 45 min., the same behavior was observed, therefore an assumption was made that the shoulder was not caused by nonequilibrium measurements.

# CHAPTER 4

# RHEOLOGY OF POLYMERS MODIFIED BY SURFACTANT

## Sol versus Gel Formation

When surfactants or polyelectrolytes are added to polymer solutions, it results in either a sol or a gel forming. The addition of electrolytes to certain moderately concentrated sols results in gelation rather than flocculation. A gel is a homogeneous-looking system, displaying some rigidity and elasticity. In the gel the particles are agglomerated to one single "floc" which extends throughout the available volume. When the particles are more or less spherical, they may be linked in "strings of beads" fashion and thus impart rigidity to the system. Plate like particles may associate to rigid "house of cards" structures, and rods or needles may build a scaffolding. The rigidity of the gel will depend on the number and the strength of the particle links in the continuous structure.[18]

## EHEC Polymer Solutions

The effect of surfactant addition to an Ethyl(hydroxyethyl) Cellulose, EHEC, polymer solution has been extensively studied.[1219] The surfactants studied were cetyltrimethylammonium bromide (CTAB), which is a cationic surfactant, and sodium dodecyl sulfate, SDS, which, as stated earlier, is an anionic surfactant. These surfactants were added at varying concentrations to EHEC and hydroxypropyl cellulose, HPC.

When SDS is added to the EHEC system, the viscosity increases compared to the EHEC solution without surfactant. With increasing temperature the viscosity also increases to a maximum before it decreases. The addition of SDS to HPC increased the viscosity relative to HPC and as temperature increased the viscosity decreased.

The addition of CTAB to EHEC increased the viscosity. The shear rate dependence was non-existent. As the temperature was increased the viscosity of the EHEC/CTAB system decreased. The molecular weight of CTAB is lower than that of SDS and CTAB is more hydrophobic than SDS. These characteristics of the surfactants explain the differences in the shear rate dependence of the two systems. The viscosity increase of SDS addition to EHEC is greater than the CTAB addition. The fact that SDS is less hydrophobic results in the higher viscosity values than those of CTAB. Newton's Law of Viscosity is valid in good approximation for the CTAB system.[19]

The polymer-surfactant systems studied at room temperature behaved as normal polymer solutions. The system transformed into a clear, stiff gel as the temperature increased. The mechanism for thermal gel formation is based on the ability for micelles to cluster on the polymer chain, and to couple with segments on other chains. The viscosity of EHEC/SDS decreased suggesting that the surfactants connected on two or more parts of the single polymer chain.

As the surfactant concentration increases, the viscosity and apparent gel forming ability of the system diminishes. This could be the result of two possible events. The first suggestion is that the number of polymer bound surfactants on each chain increases, while the probability for one aggregate to interconnect with another polymer chain decreases. A second conclusion could be that the formation of free micelles might solubilize the hydrophobic polymer to a greater extent. As the surfactant concentration increases, the properties of the polymer-surfactant system are dominated by the free micelles.[19]

Specific concentrations of the EHEC/surfactant systems were examined through a temperature range of 25 – 45 ºC. EHEC concentrations of 1, 2 and 4 wt%, were set with a constant surfactant concentration of 4mm. The surfactant concentration studied is above the critical concentration for polymer bound micelle formation. Plotting the loss tangent vs. temperature for the EHEC/surfactant systems will allow for the gel point of the system to be determined. Each system displays similar behavior in that the loss tangent decreases with increasing temperature. These measurements were made at several frequencies, and the loss tangent decrease was the most pronounced at the lowest frequency. Where the curves intersect, with each curve representing a different frequency, a gel point can be indicated. For both EHEC/surfactant systems, the gel point is the same at 1 wt% concentration. As the EHEC concentration increases the gel point shifts toward lower temperatures, and the gel point temperature is lower for the EHEC/SDS system than that of the corresponding EHEC/CTAB system.

The behavior difference between the two systems can be attributed to the idea that the physical cross-linking efficiency during the gel formation process is more temperature dependent for the anionic EHEC/SDS system than that of the cationic EHEC/CTAB system.[12] The temperature dependence of $\eta'$ and $\eta''$ during the gelation of each system is the same. The values of $\eta'$ and $\eta''$ both decrease as the temperature increases. This is an indication that as the gel forms and strengthens, the viscosity decreases. The value of $\eta'$, which is representative of the dynamic storage modulus, drops off more strongly with increasing temperature than the $\eta''$ value, which represents the dynamic loss modulus.[19]

## HPC Polymer Solutions

The interaction between the nonionic polymer HPC and the cationic surfactant hexadecyltrimethylammonium bromide (HTAB) was studied using both viscometric and dynamic light scattering.[20] It was shown that the specific viscosity of the system increases initially as HTAB is increased then reaches a peak. After the peak is reached the specific viscosity gradually decreases. The initial increase in specific viscosity can be attributed to the increase in HPC chain size due to the electrostatic repulsion between micelles bound to the polymer chain. Chain expansion continues until the number of bound micelles reaches a maximum value. This maximum value is assumed to occur where the specific viscosity reaches a maximum. The reduction in specific viscosity as more micelles were added is due to electrostatic screening from the excess $Br^-$ ions.

The amount of HTAB needed to attain maximum binding is dependent on the polymer concentration. As the polymer concentration increases the amount of HTAB needed to reach maximum binding also increases. It is also shown that the ratio of $[HTAB]_{max}/[HPC]$ varies negligibly and can be considered constant.[20]

Dynamic light scattering data of this system shows that the hydrodynamic radius, $R_h$, increases to a maximum and then decreases as more HTAB is added. This is consistent with the viscometric data, which supports the idea that as more micelles bind to an HPC chain, chain expansion occurs due to electrostatic interactions followed by chain reduction from electrostatic screening.

Comparison of the effects of cationic, anionic, and non-ionic surfactants on HPC was examined.[21] Rheological studies were performed on 1wt.% HPC solutions at 25ºC. The viscosity/shear rate curves are non-Newtonian and exhibit reversible shear thinning

flow. Further experiments show that adding 1 M NaCl to the HPC increases the viscosity relative to the salt free HPC system. The HPC/NaCl system is also non-Newtonian and shear thinning.

Four cationic surfactants, hexadecyltrimethylammonium chloride (HTAC), hexadecyltrimethylammonium bromide (HTAB), dodecyltrimethylammonium chloride (DTAC), and dodecyltrimethylammonium bromide (DTAB), were added to the HPC system and the surfactant effect on the relative viscosity was studied. For all four surfactants added at varying concentrations, the relative viscosity reaches a maximum value and then decreases. The relative viscosity of the anionic surfactant SDS was also examined. As with the cationic surfactants the relative viscosity reached a maximum and then decreased. The peak relative viscosity for the SDS system was at least five times greater than the peaks for the cationic surfactants.[21]

Two non-ionic surfactants, octaethyleneglycol mono-*n*-dodecyl ether ($C_{12}E_8$), and dodecyl-$\beta$-D-maltoside (DM), were also studied. For the HPC/$C_{12}E_8$ system the relative viscosity was unchanged upon surfactant addition until high concentrations of $C_{12}E_8$ was reached. At these higher concentrations, the increase in the relative viscosity was equal to 0.33, which is minimal. The addition of DM to HPC had no effect on the relative viscosity of the HPC.[21]

At elevated concentrations, intermolecular interactions dominate the rheology of aqueous polymer solutions. Since the 1wt.% aqueous HPC solution is non-Newtonian and displays reversible shear-thinning flow behavior, a degree of intermolecular entanglement can explain these characteristics. The viscosity of polyelectrolytes, whose degree of ionization can be altered, increases with the surface charge density. The

viscosity increase can be attributed to the uncoiling of the polyelectrolyte, and the resultant increased interaction between the polyelectrolyte molecules. The viscosity decrease with increasing shear rate has been attributed to the reduction in the amount of "three dimensional network structure" in the polyelectrolyte system.[21]

It has been a belief that surfactant adsorption can occur below the critical micelle concentration, CMC, and is a cooperative process. This means that surfactant molecules self-assemble on the polymer chain to form aggregates, which are smaller in size than bulk micelles. As the aggregates accumulate on the polymer chain, the cloud point and rheological properties begin to change. As more surfactant is added to the polymer system, a point is reached where bulk micelles form.[21]

As the number of aggregates on the polymer chain increases, the polymer chains may stretch out in response to the inter-aggregate electrostatic repulsion. The increases in the adsorbed surfactant aggregates causes the effective volume occupied by the HPC molecules in the solution to increase. The relative viscosity and relative shear parameter results indicate that the bulk micelles break up the "three-dimensional polymer structure". At high concentrations the relative shear parameters in the HTAB and HTAC systems are less than that in the aqueous 1wt.% HPC solution.

## HPMC Polymer Solutions

The interaction between hydroxypropylmethyl cellulose, HPMC, and SDS has also been studied.[22] Reduced specific viscosity was measured against SDS concentration at specific HPMC concentrations. The HPMC concentrations were set at 0.05, 0.1, 0.2, and 0.3% HPMC. For all four HPMC concentrations three distinct regions appeared in the viscosity vs. SDS concentration curves. In region I, low SDS concentration (0 – 4

mM), the viscosity was insensitive to SDS. No HPMC-SDS interaction was observed. In region II, moderate SDS concentrations (4 – 12mM), the viscosity was very sensitive to the SDS concentration. The 0.05 and 0.1% HPMC solutions show that the viscosity goes to a minimum, while the 0.2 and 0.3% HPMC solutions show that the viscosity passes through a maximum. Region III consists of high SDS concentration (> 12mM). In this region the viscosity becomes insensitive to [SDS], and all four HPMC concentrations approach the same viscosity value.[22]

Amphiphilic materials display characteristics of both hydrophilic and hydrophobic molecules. Amphiphilic compounds are also known as surfactants. If a small amount of amphiphilic material is mixed with water, it is possible for the molecules to go into solution. As the amphiphilic concentration increases, one of two possible structures begins to form. If the molecule has a strong polar head group relative to the nonpolar tail, the amphiphilic molecules begin to form spheres, with the polar head groups on the outside, and the nonpolar tails pointed inward. This structure is called a micelle and it is stable as long as the amount of amphiphilic material is above a certain concentration, the critical micelle concentration, CMC.

If the head group is not strong relative to the tail, the molecules begin to form spherical vesicles, where double layers of amphiphilic molecules, called bilayers, form a shell with water on the inside and outside.

If the surfactant concentration increases, more micelles or vesicles form. In some cases the size and shape of the micelles or vesicles remain fairly constant as their numbers increase. In other cases the shape of the micelles change from spherical to cylindrical. The vesicles can form several bilayers. If the concentration of the amphiphilic

material is increased even more, up to 50%, a point is reached where the micelles or vesicles combine to form larger structures, which are liquid crystalline.[23] There are three types of these structures, which are the hexagonal phase, the lamellar phase, and the cubic phase. The hexagonal phase is a structure in which long cylindrical rods of amphiphilic molecules arrange the long axes of the rods in a hexagonal array. The lamellar phase, which occurs at higher concentrations than the hexagonal phase, has a structure in which the amphiphilic molecules form flat bilayers separated from each other by water. The cubic phase is a less common phase and forms at concentrations between the hexagonal and lamellar phases. The cubic phase is composed of spheres of amphiphilic molecules that arrange themselves in a cubic lattice.

Amphiphilic compounds first form micelles and then the various liquid crystal phases as the concentration of the amphiphilic material increases. If the temperature is high enough, the sequence is quite different as the concentration of the amphiphile increases. At very low concentrations, micelles form as usual, but at a certain concentration they break up and the system forms two separate phases, one rich in water and the other rich in amphiphile. If the concentration is further increased, the micelles again form and the two separate phases combine to form the usual homogeneous phase of water and micelles. At these higher temperatures, a region exists where the two components cannot be mixed, and is called the miscibility gap. This miscibility gap shows just how delicate the balance is for the formation of micelles in the amphiphile/water system.

# CHAPTER 5

# MATERIALS AND METHODS

## Materials

Hydroxypropyl cellulose, average $M_w = 10^6$ and sodium dodecyl sulfate FW = 288.38 were both purchased from Aldrich (http://www.sigmaaldrich.com/). Dissolving the powdered polymer into distilled water made hydroxypropyl cellulose, HPC, solutions. Each solution was made by weight ratios. Sodium dodecyl sulfate, SDS, solutions were prepared by dissolving the SDS powder into distilled water to 10 critical micelle concentration, CMC. Subsequent concentrations were made by water dilution. HPC/SDS gels were prepared by mixing the HPC and SDS solutions resulting in the sample gels.

## Methods

All rheological measurements were performed on a Paar Physica Universal Dynamic Spectrometer (UDS200)( http://www.paarphysica.com/). A peltier thermal unit was used for temperature control, which was coupled to a water recirculator kept constantly at 15 degrees C. The measuring configuration was a cone and plate with the cone having a working diameter of 50 millimeters and a measuring angle of 2 degrees. The initial measurement consisted of a strain amplitude sweep at 30 degrees C, to determine the linear region. The results are shown in Figures 1 and 2. Based on the results, a constant strain of 0.2 was used for all the viscosity – frequency-temperature measurements. The initial step of the measurement allowed for the sample to reach equilibrium by letting the sample be placed under constant strain and frequency for five minutes. This was followed by four data points taken twenty seconds apart. The sample gel was then heated for two minutes, and data points for the resultant temperature were

taken. A new sample was inserted for each temperature and frequency reported in the paper.

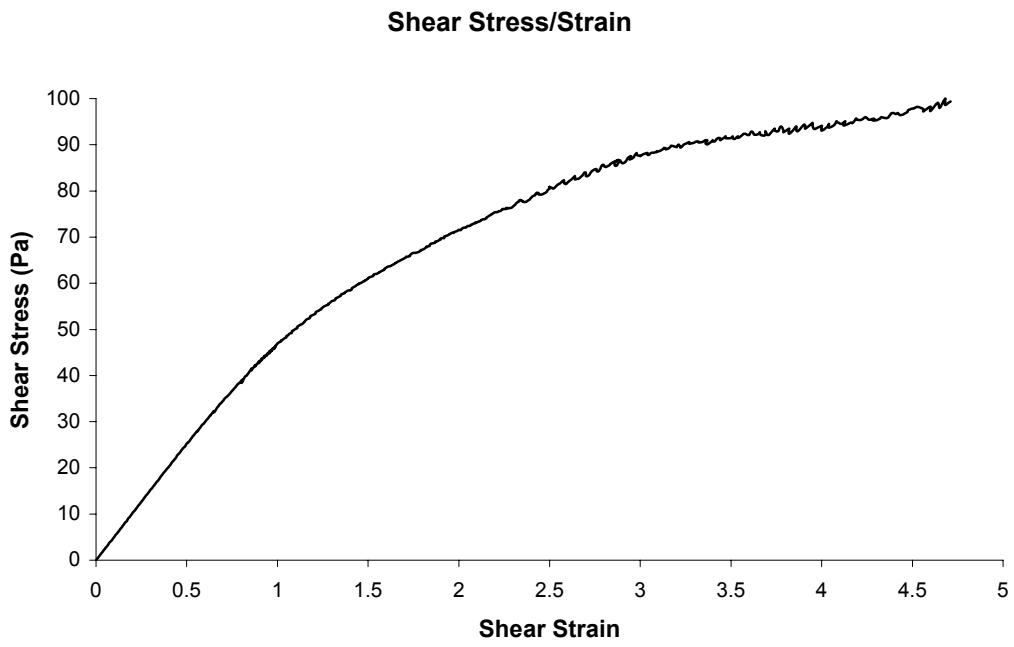


**Figure 1: Shear stress/strain curve.**

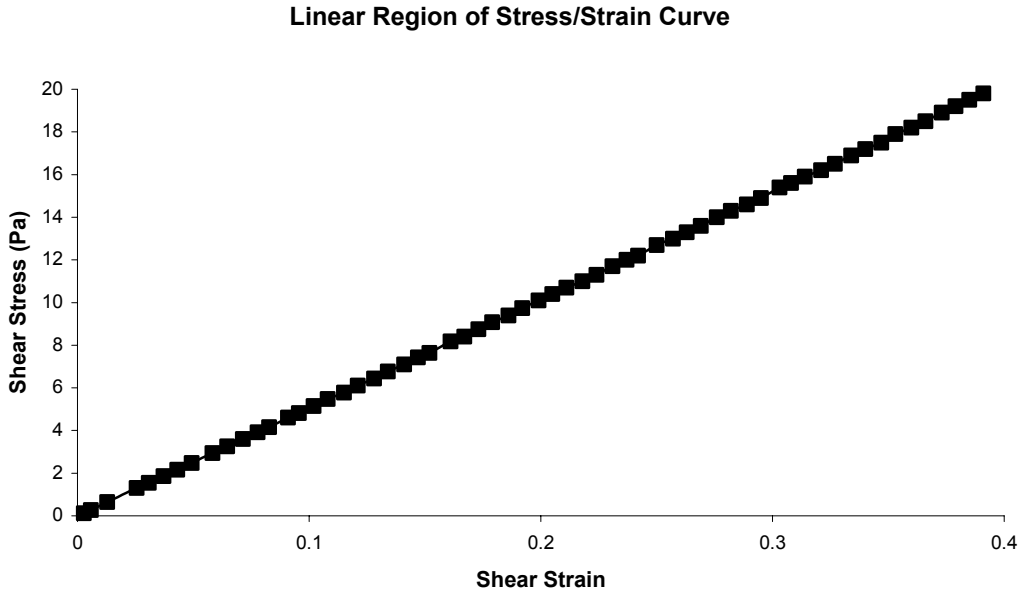


**Figure 2: Linear region of the shear stress/strain curve seen in figure 1.**

CHAPTER 6

RESULTS

Looking at the viscosity changes involved in the HPC percentage increase can give an insight into the resultant gels when the SDS is added. Figures 3 and 4 both show that at varying frequencies the 1% and 2% HPC solutions are Newtonian in behavior. The 4% and 8% HPC solutions show biphasic characteristics. This is due to the sharp decrease in viscosity at around 40C. Figures 4 and 5 both show that the storage modulus behaves in the same manner as the viscosity for the HPC solutions.

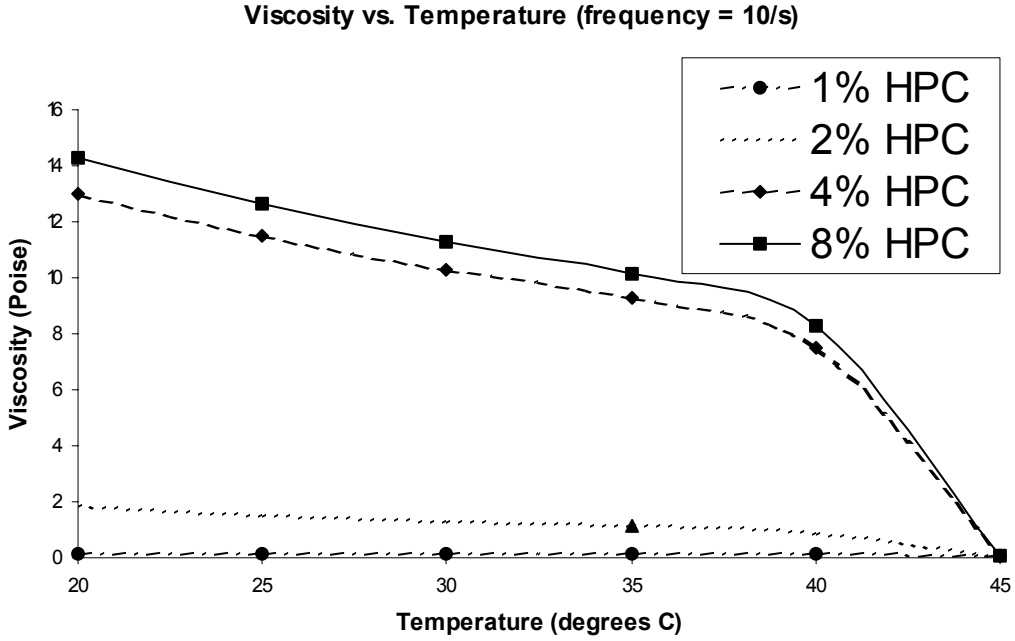


**Figure 3: The Newtonian behavior of the 1% and 2% HPC solutions at a frequency of 10/s are seen as well as the biphasic nature of the 4% and 8% HPC solutions at the same frequency**.

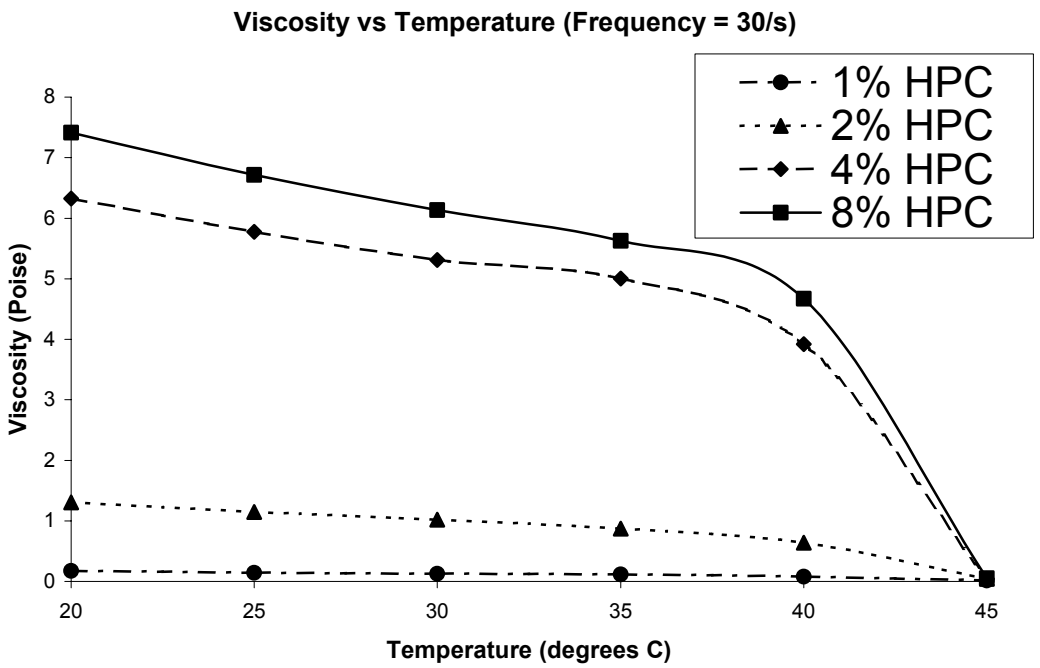


**Figure 4: The Newtonian behavior of the 1% and 2% HPC solutions at a frequency of 30/s are seen as well as the biphasic nature of the 4% and 8% HPC solutions at the same frequency.**

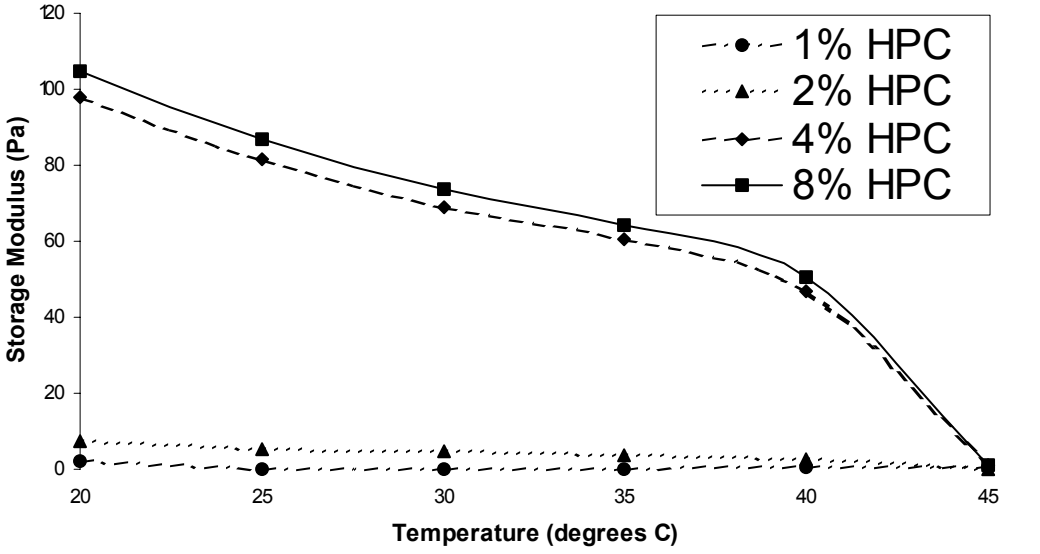


**Figure 5: The storage modulus of the 1% and 2% HPC solutions at a frequency of 30/s also is Newtonian in behavior. The 4% and 8% HPC solutions behave as biphasic solutions at the same frequency.**

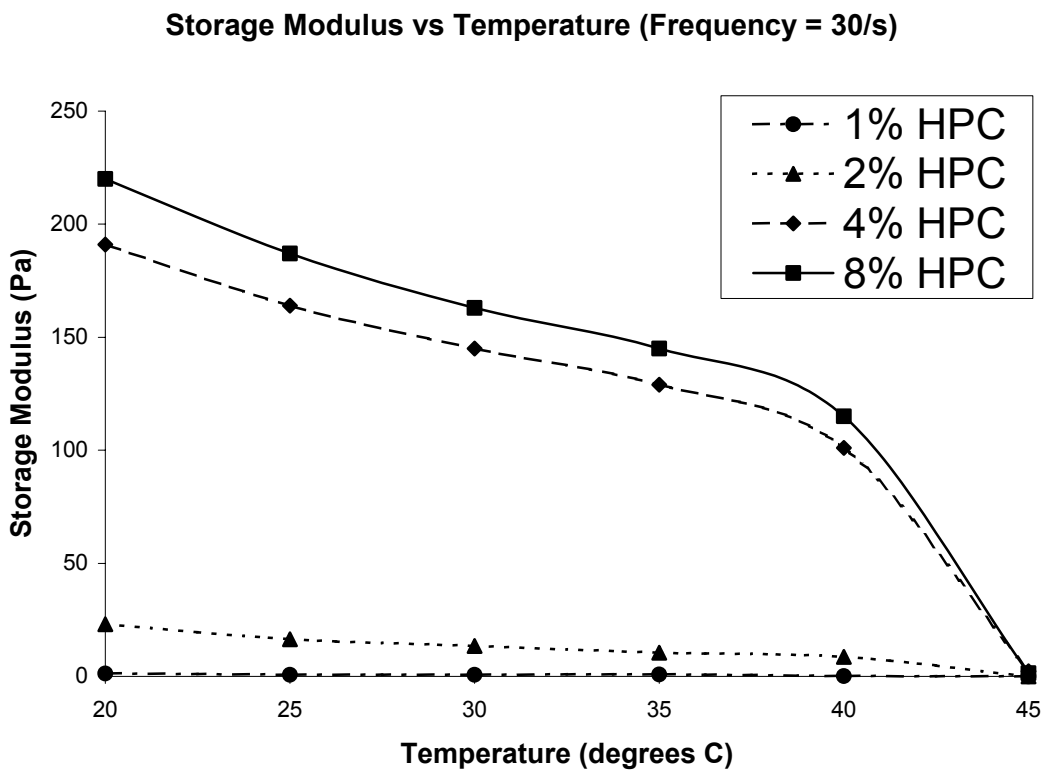


**Figure 6: The storage modulus of the 1% and 2% HPC solutions at a frequency of 30/s also is Newtonian in behavior. The 4% and 8% HPC solutions behave as biphasic solutions at the same frequency.**

Plotting the relative viscosity vs. the Log[SDS] of the 2% gels (Figures 7 and 8) show that as frequency increases the viscosity decreases. The viscosity also decreases as the temperature increases. The peak CMC of the surfactant shifts to the left as the temperature increases. Figures 9 and 10 show the storage modulus behavior plotted against the log [SDS]. Modulus increases as frequency increases and decreases as temperature decreases.

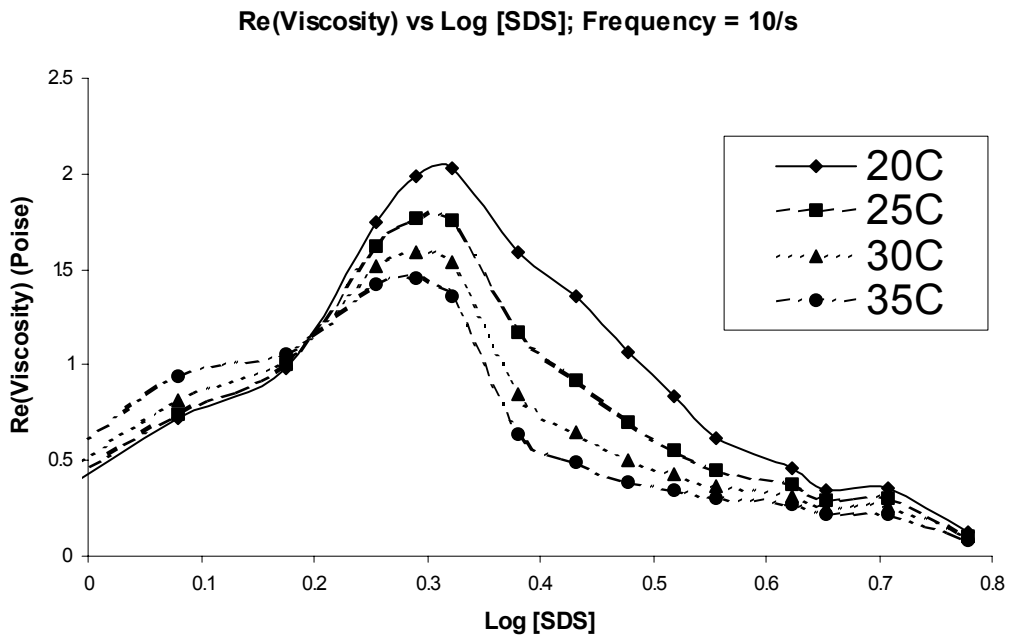


**Figure 7: Plot of the relative viscosity vs. the log of the SDS concentration at varying temperatures and at a frequency of 10/second.**

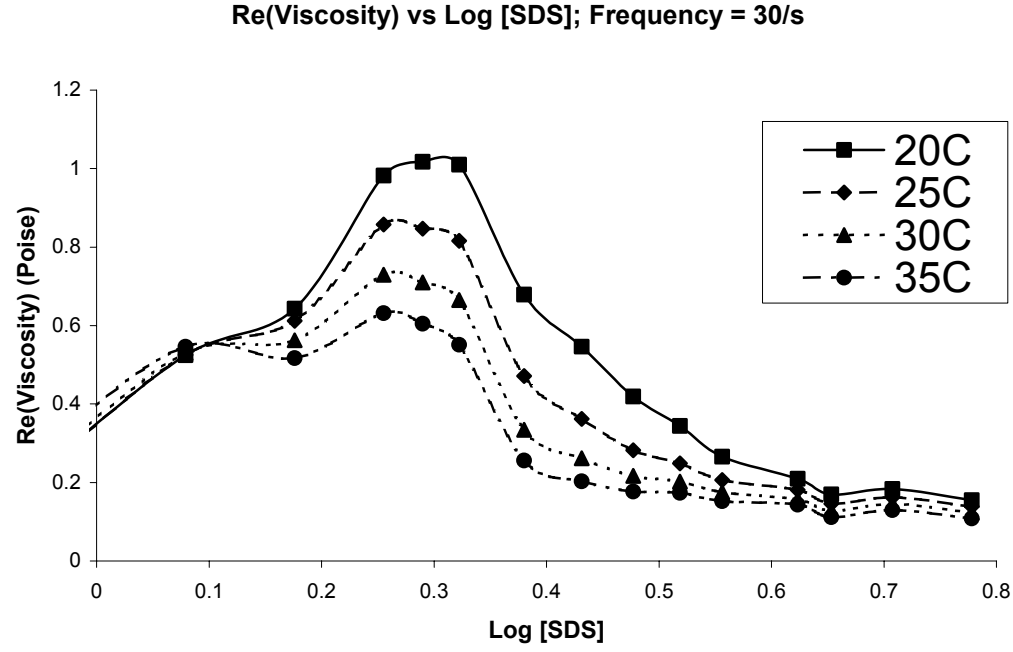


**Figure 8: Plot of the relative viscosity vs. the log of the SDS concentration at varying temperatures and at a frequency of 30/second.**

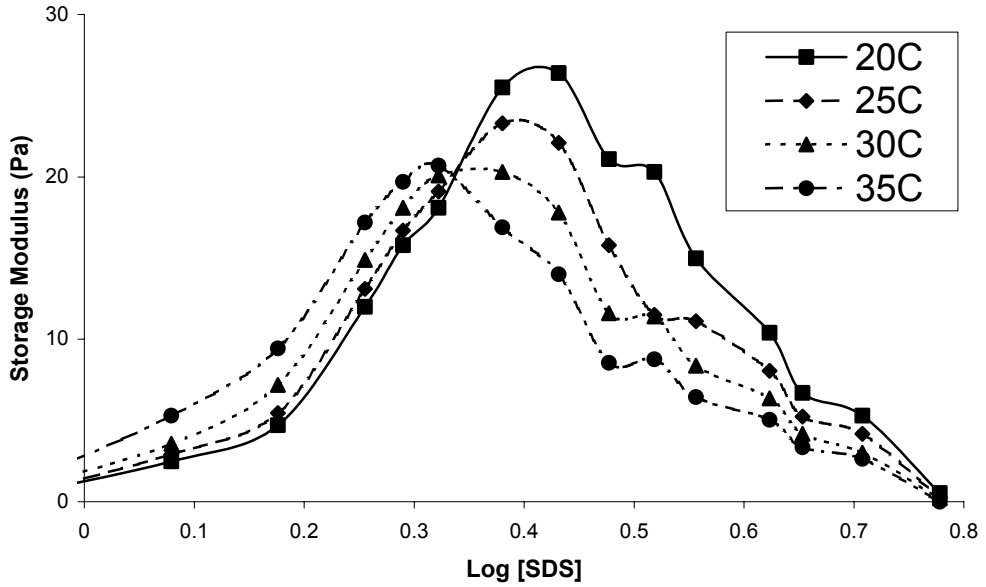


**Figure 9: Plot of the storage modulus vs. the log of the SDS concentration at varying temperatures and at a frequency of 10/second.**

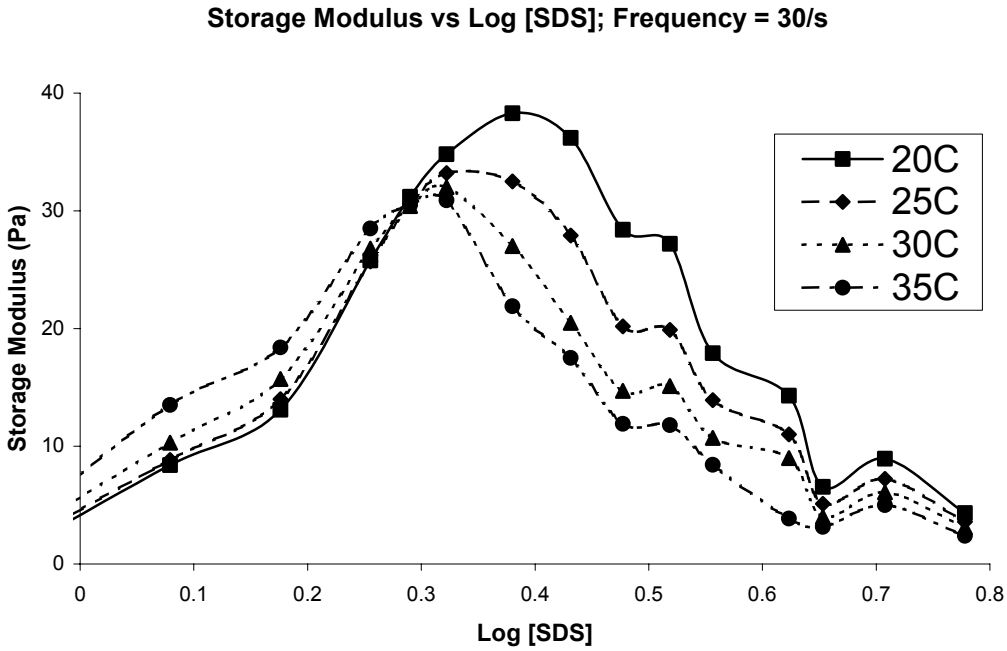


**Figure 10: Plot of the storage modulus vs. the log of the SDS concentration at varying temperatures and at a frequency of 30/second.**

Figure 11 shows how the storage modulus of the gel behaves as a function of temperature. As the SDS concentration increases the modulus increases up to the peak CMC of the gel, where the modulus starts to decrease. The behavior is the same at increased frequency, and both frequencies show that the peak CMC (SDS concentration) is about 0.7CMC.

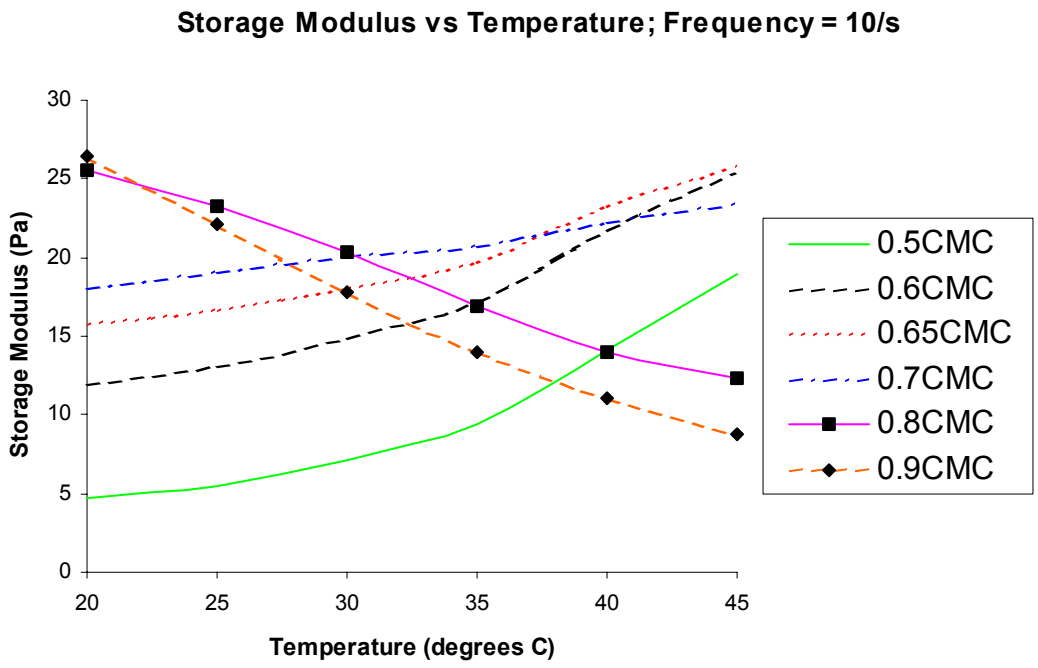


**Figure 11: Using the data in this plot, gels of certain stiffness could be formulated. The higher the storage modulus the more stiff a gel becomes.**

Reviewing Figures 12 and 13 show how the HPC concentration increase dramatically alters the viscosity and modulus of the resultant gels. At a frequency of 10radians/sec, the viscosity increase from 2% to 8% HPC of the 0.4CMC gel is 69%, 63% for the 0.7CMC gel, and 89% for the 1.0CMC gel. The storage modulus increase from the 2% to the 8% HPC gels is 68% for 0.4 CMC, 42% for 0.7 CMC and 77% for the 1.0 CMC gel.

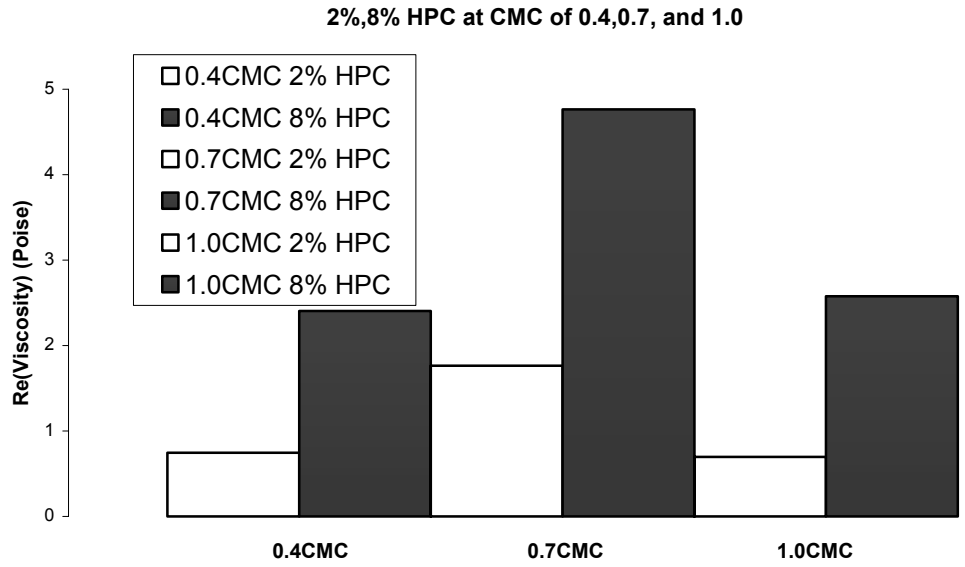


**Figure 12: Comparison of the relative viscosity of 2% and 8% HPC gels at varying critical micellular concentrations (CM). Frequency = 10/s and temperature is set at 25°C.**

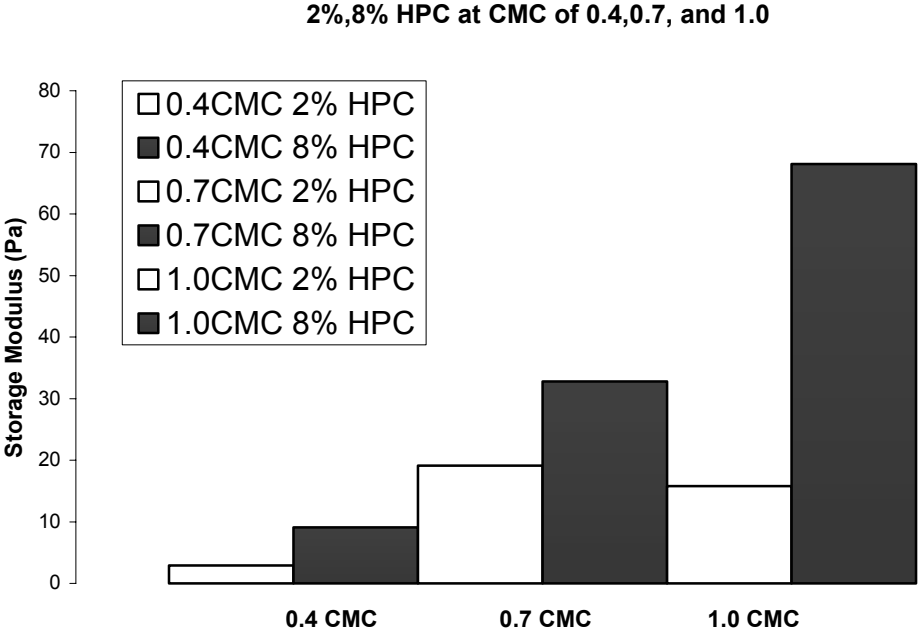


**Figure 13: Comparison of the storage modulus of 2% and 8% HPC gels at varying critical micellular concentrations (CM). Frequency = 10/s and temperature is set at 25°C.**

# CHAPTER 7

# CONCLUSION

The rheological behavior of low concentration SDS/ HPC gel systems is different than that of the more widely studied higher concentration systems. Data shows that the low polymer concentration gels do not necessarily follow the trends of the higher polymer concentration gels. The 1% and 2% polymer concentration solutions behaved markedly different than did the 4% and 8% polymer concentration solutions. (See Figures 3 – 6) Subsequent data shows that the storage modulus of the HPC polymer solution increases with increasing frequency. The relative viscosity of the same system decreases with increasing frequency. Both the storage modulus and viscosity decrease with increased temperature is dependent on both temperature and gel concentration.

REFERENCE LIST

(1) Liu, S., Masliyah, J. H. *Suspensions: Fundamentals and Applications in the Petroleum Industry*; Schramm, L. L., Eds.; American Chemical Society: Washington DC, 1996.

(2) Dealy, J. M., Wissbrun, K. F. *Melt Rheology and its Role in Plastics Processing*; Chapman and Hall: London, 1995.

(3) Carreau, P. J., De Kee, D. C. R., Chabra, R. P. *Rheology of Polymeric Systems*; Hanser/Gardner Publications, Inc.: Cincinnati, 1997.

(4) Macosko, C. W. *Rheology: Principles, Measurements, and Applications*; Wliey-VCH, Inc.: New York, 1994.

(5) Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials 2nd Edition;* Blackie Academic & Professional: Glasgow, 1991.

(6 ) Jones, D. S.; Woolfson, A. D.; Brown, A. F." Textural, Viscoelastic and Mucoadhesive Properties of Pharmaceutical Gels Composed of Cellulose Polymers", *International Journal of Pharmaceutics,* **1997**, 151, pp. 223-233.

(7) Jones, D. S.; Woolfson, A. D.; Djokic, J.; Coulter, W. A. "Development and Mechanical Characterization of bioadhesive Semi-solid Polymeric Systems Containing Tetracycline for the Treatment of Periodontal Disease", *Pharmacological Research,* **1996a**, 13, pp. 1732-1736.

(8) Jones, D. S.; Woolfson, A. D.; Djokic, J." Texture Profile Analysis of Bioadhesive Polymeric Semisolids: Mechanical Characterization and Investigation of Interactions Between Formulation Components", *Journal of Applied Polymer Science,* **1996b**, 61 (12), pp. 2229-2234.

(9) Barry, B. W."Rheology of Pharmaceutical and Cosmetic Semisolids", In *Advances in Pharmaceutical Sciences*; Bean, H. S., Beckett, A. H., Carless, J. E., Eds.; Academic Press: London, **1974**; Vol. 4, pp. 1-72.

(10) Barry, B. W.; Meyer, M. C. "The Rheological Properties of Carbopol Gels. II> Oscillatory Properties of Carbopol Gels", *International Journal of Pharmacy,* **1979b**, 2, pp. 27-40.

(11) Davis, S. S. "Viscoelastic Properties of Pharmaceutical Semisolids. III. Nondestructive Oscillatory Testing", *Journal Pharmaceutical Sciences*, **1971**, 60, pp. 1351-1356.

(12) Carlsson, A.; Karlström, G.; Lindman, B. "Thermal Gelation of Nonionic Cellulose Ethers and Ionic Surfactants in Water", *Colloids and Surfaces,* **1990**, 47, pp. 147-165.

(13) Grizzuti, N.; Cavella, S.; Cicarelli, P.” Transient and Steady-State Rheology of a Liquid Crystalline Hydroxypropylcellulose Solution”, *Journal of Rheology,* **1990**, 34 (8), pp. 1293-1310.

(14) Smyth, S.; Mackay, M.” The Viscous Stress Contribution to Lyotropic Hydroxypropylcellulose Solutions in the Biphasic and Liquid-Crystalline Regions”, *Journal of Rheology,* **1994**, 38 (5), pp.1549-1558.

(15) Baek, S.; Magda, J.; Cementwala, S.” Normal Stress Differences in Liquid Crystalline Hydroxypropylcellulose Solutions”, *Journal of Rheology,* **1993**, 37 (5), pp. 935-945.

(16) Hongladarom, K.; Secakusuma, V.; Burghardt, W.” Relation Between Molecular Orientation and Rheology in Lyotropic Hydroxypropylcellulose Solutions”, *Journal of Rheology,* **1994**, 38 (5), pp. 1505-1523.

(17) Goldszal, A.; Jamieson, A.; Mann Jr., A.; Polak, J.; Rosenblatt, C.” Rheology, Optical Microscopy, and Electron Microscopy of Cationic Surfactant Gels”, *Journal of Colloid and Interface Science,* **1996**, 180 (1), pp. 261-269.

(18) van Olphen, H. *An Introduction to Clay Colloid Chemistry*; John Wiley & Sons, Inc.: New York, 1963.

(19) Nystrom, B.; Walderhaug, H.; Hansen, F.” Rheological Behavior During Thermoreversible Gelation of Aqueous Mixtures of Ethyl(hydroxyethyl)cellulose and Surfactants”, *Langmuir,* **1995**, 11 (3), pp. 750-757.

(20) Hormnirun, P.; Sirivat, A.; Jamieson, A.” Complex Formation Between Hydroxypropylcellulose and Hexadecyltrimethylamonium Bromide as Studied by Light Scattering and Viscometry”, *Polymer,* **2000**, 41 (6), pp. 2127-2132.

(21) Drummond, C.; Albers, S.; Furlong, D.”Polymer-Surfactant Interactions: (Hydroxypropyl)cellulose with Ionic and Ion-ionic Surfactants”, *Colloids and Surfaces,* **1992**, 62 (1-2), pp. 63-73.

(22) Nilsson, S.” Interactions between Water-Soluble Cellulose Derivatives and Surfactants. 1. The HPMC/SDS/Water System”, *Macromolecules* **1995**, 28 (23), pp. 7837-7844.

(23) Collings, P. J. *Liquid Crystals*; Princeton University Press: Princeton, NJ, 1990.